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V. *An Account of some new Experiments on the fluoric Compounds ;
with some Observations on other Objects of Chemical Inquiry.*
By Sir H. Davy, LL.D. F.R.S. V. P. R. I.

Read February 13, 1814.

IN this Paper I shall offer to the Society a continuation of those researches, the details of which have been already honoured with a place in their Transactions ; and I trust, that the experiments and observations which I have to communicate, will be found to elucidate some important but obscure parts of chemical philosophy.

In the last Paper, which I had the honour of presenting to this Body, I have given an account of a number of experiments made with a view of decomposing the fluoric acid: the most probable inference, from my results, was that the pure liquid fluoric acid consists of hydrogen united to a substance, which, from its strong powers of combination, has not as yet been procured in a separate form, but which is detached from hydrogen by metals, and which, in union with the basis of the boracic acid and silica, forms the fluo-boric and silicated fluoric gases.

All the new experiments, that I have made on the fluoric compounds, tend to confirm this idea ; and the various attempts that I have made, since the last session, to decompose the principle in the fluoric acid separated at the negative surface in Voltaic combinations, have been unsuccessful.

I have found that fluuate of lead, the substance formed by

the action of a soluble salt of lead on fluuate of potassa or fluuate of ammonia, is immediately decomposed, when moist, by ammoniacal gas, and a white powder separates from it, which must contain oxygen, as it gives carbonic acid by being ignited with charcoal; but dry fluuate of lead may be fused in ammonia without undergoing the slightest alteration, and the presence of water, which may furnish oxygen to the lead and hydrogen to the fluoric principle, seems absolutely necessary for the production of oxidated bodies from the fluoric combinations.

I obtained analogous results by acting on silicated fluuate of ammonia and fluo-borate of ammonia by chlorine; when the salts were moist, or when the gas was not free from vapour, silica and boracic acid were formed in small quantities, but when water was carefully excluded, these bodies did not appear; and the results were muriate of ammonia and silicated fluoric gas, or fluo-boric gas and azote.

I ignited two points of charcoal intensely in fluo-boric and silicated fluoric acid gases, pure, and mixed with oxygen; but no change, indicating a decomposition, took place; the only new product was a little inflammable gas, which was probably disengaged from the charcoal.

I passed pure liquid fluoric acid over charcoal ignited to whiteness, in a platinum tube; no carbonic acid was formed, and a very minute quantity of gas only was produced, which proved to be hydrogen.

I mentioned in my last communication to the Society, that I had made several experiments on the composition of the fluates; since that time I have repeated some of the processes, and I shall detail such of the results as appear to be most

correct. In experiments on the fluates, it is very difficult to exclude sources of inaccuracy; glass vessels cannot be used, and even silver and platinum vessels are slightly acted upon by the pure fluoric combinations soluble in water.

Fluor spar decomposed by sulphuric acid increases more than three-fourths of its original weight; but to produce this result several successive distillations of it with fresh portions of acid are necessary, and the spar must be in very fine powder, and the result must be powdered after every operation.

In an experiment made in a crucible of platinum, in which very pure white Derbyshire spar was used, and sulphuric acid distilled in glass vessels, and in which the product was heated to whiteness in every operation, 100 grains became in the first operation 159.4 grains, which gained

in the second	-	6.9
in the third	-	4.2
in the fourth	-	1.9
in the fifth	-	1.6
in the sixth	-	0.9
in the seventh	-	0.3
in the eighth	-	0.0
Total increase	-	75.2

If this result be calculated upon, supposing the number representing calcium to be 40, as I have given it in my *Elements of Chemical Philosophy*, the number representing fluorine will be 34.2, and fluor spar must be supposed to be composed of 40 calcium, and 34.2 fluorine.

22 grains of fused subcarbonate of potassa decomposed by diluted liquid fluoric acid, in an experiment made with great care, was found to afford 18.15 grains of dry fluuate of potassa;

and by a very careful analysis, it was found that this subcarbonate contained 31 per cent. of carbonic acid; now, if the remainder of the salt be supposed to be pure potassa, and the calculations be made on this idea, it will appear that fluuate of potassa must consist of 125.9 of potassium and 54.74 of fluorine, and the number representing fluorine must be regarded as 32.6.

The 18.15 grains of fluuate of potassa decomposed by sulphuric acid afforded 38.5 of acid sulphate of potash. Supposing acid sulphate of potassa to consist of two proportions of sulphuric acid 150, and one of potassa 90, they ought to have given 40 grains, and this loss is no more than might be expected in the process of decomposition and evaporation.

In some experiments that I made on the decomposition of the hydrates of potassa and soda, when decomposed by fluoric acid, the results indicated a number for fluorine a little lower. Thus 20 grains of hydrate of potassa were converted into 19.8 grains of fluuate of potassa, and 20 grains of hydrate of soda into 19.6 of fluuate of soda; but I do not place so much confidence in these results, as there always was great heat produced during the action of the acid upon the hydrates; and probably a minute quantity of the hydrates might have been dissipated at the beginning of the process.

It appears reasonable to conclude, as I have stated in my last paper, published in the Philosophical Transactions, that the number representing fluorine is less than half of that representing chlorine, about 33.

I endeavoured to ascertain the composition of fluuate of ammonia, by adding together hydro-fluoric acid and solution of ammonia of known composition, and I found in this way, that

100 parts of solution of ammonia of specific gravity 9162 required for its saturation 52 grains of diluted fluoric acid of such a strength, that an equal portion produced exactly 32 grains of fluato of potassa. According to this experiment fluato of ammonia must consist of 9.7 of fluorine to 22 of ammonia;* and, if it be conceived that liquid fluoric acid consists of two proportions of hydrogen to one of fluorine, the true composition of fluato of ammonia will be one proportion of fluoric acid 35, and two proportions of ammonia 64.†

The volatility of fluato of ammonia rendered it impossible to ascertain by evaporation the real quantity of solid salt formed, though the heat was never raised so high as that of boiling water, yet only 12.7 grains of solid fluato of ammonia could be procured.

Two hundred cubical inches of ammonia, which weigh 36 grains, condense one hundred cubical inches of silicated fluoric gas, weighing, under the same circumstances, 110.7, and if it be supposed that silicated fluato of ammonia contains one proportion of silicated fluoric acid and one of ammonia, then the number representing silicated fluoric gas will be 98.4, and it may be conceived to consist of two proportions of fluorine 66, and one of the siliceous basis 32.4.

According to the experiments of JOHN DAVY, 100 parts of silicated fluoric acid afford 61.4 of silica when decomposed by aqueous solution of ammonia, hence silica may be conceived to consist of 32.4 of basis and 29 of oxygen, and this is very near two proportions of oxygen.

* See Elements of Chemical Philosophy, page 268.

† That is, if ammonia be regarded as composed of one proportion of azote 26, and six of hydrogen.

I decomposed 20 grains of silicated fluat of ammonia by solution of ammonia, and I obtained 9.2 grains of silica. This result offers proportions very little different from those gained in the preceding calculations.

I have made some direct experiments with the hopes of determining the proportions of oxygen in silica, but they have been unsuccessful; I have ascertained, however, that it requires more than three parts of potassium to decompose one part of silica, which shews that this substance cannot contain much less than half its weight of oxygen.

I have endeavoured to separate the siliceous basis in a pure form, with the view of making synthetical experiments on its nature by combustion in oxygen, and my results, though not perfectly satisfactory, yet seem worthy of notice, and may lead to more successful attempts.

I decomposed silica by passing potassium in excess through it, in a heated tube of platinum: the result consisted chiefly of alkali containing a dark coloured powder, the basis of silica diffused through it. I fused the whole mass with sulphur, which, in combining with the dry alkali, produced ignition. I attempted to detach the sulphuret of potassa by water: in this case the dark particles separated, but during their separation and after, they acted upon the water of the solution producing gas, and, in attempting to collect them by the filter, I failed to procure sufficient for examination, for they were principally converted into silica.

I heated the substance procured in another experiment of this kind with hydrate of potassa; in this case there was a copious effervescence, and silica appeared to be reproduced and dissolved by the alkali.

I heated a portion of a similar result in strong lixivium of potassa; the solution gained a tint of olive, but there was scarcely any effervescence; from this it seems probable, that the inflammable basis of silica, like boron, is soluble in alkaline solutions without decomposing them.

Indeed this body, in its general characters, appears very analogous to boron. It appears to be neither volatile nor fusible; its oxide exerts, like boracic acid, a neutralizing power on the alkalies, though of a feebler kind, and forms, like boracic acid, vitreous bodies with the alkaline earths, and, like boron, the siliceous basis in combination with fluorine constitutes a powerful acid.

In my first views of the nature of the boracic and siliceous bases, I thought it probable that they would both appear as metals, if they could be entirely freed from oxygen; but it now seems more probable, that they form a class by themselves, offering a kind of link in the chain of natural bodies, when arranged according to their analogies, between charcoal, and sulphur and phosphorus.

It seems worthy of an experimental inquiry, whether the siliceous basis may not be obtained pure by heating the result procured from silica by potassium with pure sulphuric acid, which might possibly detach the potassa to form acid sulphate of potassa, without being decomposed by the inflammable basis.

I have made many new experiments with the hope of decomposing chlorine, but they have been all unavailing; nor have I been able to gain the slightest evidence of the existence of that oxygen which many persons still assert to be one of its elements.

I kept sulphuret of lead for some time in fusion in chlorine, the results were sulphurane (Dr. THOMSON'S liquor) and plumbane (muriate of lead); not an atom of sulphate of lead was formed in the experiment, though if any oxygen had been present, this substance might have been expected to have been produced.

I heated plumbane (muriate of lead) in sulphurous acid gas, and likewise in carbonic acid gas, but no change was produced; now, if oxygen had existed either in chlorine, or in its combination with lead, there is every reason to believe, that the attractions of the substances concerned in these experiments would have been such as to have produced the insoluble and fixed salts of lead, the sulphate in the first case, and the carbonate in the second.

I shall not enter into any discussion upon the experiments in which water is said to be produced by the action of muriatic gas on ammonia: there is, I believe, no enlightened and candid person, who has witnessed the results of processes in which large quantities of muriate of ammonia, made by the combination of the gases in close vessels, have been distilled, without being satisfied, that there is no more moisture present, than the minute quantity which is known to exist in the compound vapours diffused through ammoniacal and muriatic acid gases, which cannot be considered either as essential to the existence of the gases, or as chemically combined with them.*

* Dr. HENRY found it very difficult to free ammonia from the aqueous vapour existing in it by hydrate of potassa, and probably the hydrated muriatic vapour which I have detected in muriatic acid gas, by a freezing mixture, is not decomposable by muriate of lime.

One of the first experiments that I made, with the hope of detecting oxygen in chlorine, was by acting upon it by ammonia, when I found that no water was formed, and that the results were merely muriate of ammonia and azote;* and the driest muriate of ammonia, I find, when heated with potassium, converts it into muriate of potassa, which result would be impossible on the hypothesis of oxymuriatic gas being a compound of oxygen, for, if there was a separation of water during the formation of the muriate, the same oxygen could not be supposed to be detached in water, and yet likewise to remain so as to form part of a neutral salt.

If water had been really formed during the action of chlorine on ammonia, the result would have been a most important one: it would have proved either that chlorine or azote was a compound, and contained oxygen, or that both contained this substance; but it would not have proved the existence of oxygen in chlorine, till it had been shewn that the azote of the ammonia was unchanged in the operation.

Some authors continue to write and speak with scepticism on the subject, and demand stronger evidence of chlorine being undecomposed. These evidences it is impossible to give. It has resisted all attempts at decomposition. In this respect, it agrees with gold, and silver, and hydrogen, and oxygen. Persons may doubt, whether these are elementary bodies; but it is not philosophical to doubt, whether they have not been resolved into other forms of matter.

By the same mode of reasoning, as that in which oxygen is conceived to exist in chlorine, any other species of matter might be supposed to form one of its constituent parts; and

* Philosophical Transactions for 1810.

by multiplying words all the phenomena might be satisfactorily explained. Thus in the simple view of the formation of muriatic acid, it is said one volume of chlorine combines with one of hydrogen, and they form two volumes of muriatic acid gas. In the hypothesis of chlorine containing oxygen, it is said, the oxygen of the chlorine combines with the hydrogen to form water, and this water unites to an unknown something, or dry muriatic acid, to produce a gaseous body. If it were asserted that chlorine contained azote, oxygen, and this unknown body, then it might be said, that, in the action of hydrogen on chlorine, the azote, the oxygen and the chlorine, having all attractions for hydrogen, enter into union with it, and form a quadruple compound.

Professor BERZELIUS has lately adduced some arguments, which he conceives are in favour of chlorine being a compound of oxygen from the laws of definite proportions; but I cannot regard these arguments of my learned and ingenious friend as possessing any weight. By transferring the definite proportions of oxygen to the metals, which he has given to chlorine, the explanation becomes a simple expression of facts; and there is no general canon with respect to the multiples of the proportions in which different bodies combine. Thus azote follows peculiar laws in combining with every different body; it combines with three volumes of hydrogen, with half a volume of oxygen, with 1.2 and $1\frac{1}{2}$ of the same body, and with four volumes of chlorine.

The chemists in the middle of the last century had an idea, that all inflammable bodies contained phlogiston or hydrogen. It was the glory of LAVOISIER to lay the foundations for a sound logic in chemistry, by shewing that the existence of

this principle, or of other principles, should not be assumed where they could not be detected.

In all cases, in which bodies support combustion or form acids, oxygen has been supposed by the greater number of modern chemists to be present; but as there are many distinct species of inflammable bodies, so there may be many distinct species of matter which combine with them with so much energy, as to produce heat and light; and various bodies appear capable of forming acids; thus hydrogen enters into the composition of nearly as many acids as oxygen, and three bodies, namely, sulphuretted hydrogen, muriatic acid, and fluoric acid which contain hydrogen, are not known to contain oxygen. The existence of oxygen in the atmosphere, and its action in the economy of nature, and in the processes of the arts, have necessarily caused it to occupy a great portion of the attention of chemists, and, being of such importance, and in constant operation, it is not extraordinary, that a greater number of phenomena should be attributed to it, than it really produces.

In the views that I have ventured to develope, neither oxygen, chlorine, or fluorine, are asserted to be elements; it is only asserted, that, as yet, they have not been decomposed.

As the investigation of nature proceeds, it is not improbable, that other more subtile bodies belonging to this class will be discovered, and perhaps some of the characteristic differences of those substances, which apparently give the same products by analysis, may depend upon this circumstance.

The conjecture appears worth hazarding, whether the carbonaceous matter in the diamond may not be united to an extremely light and subtile principle of this kind, which has

hitherto escaped detection, but which may be expelled, or newly combined, during its combustion in oxygen. That some chemical difference must exist between the hardest and most beautiful of the gems and charcoal, between a non-conductor and a conductor of electricity, it is scarcely possible, notwithstanding the elaborate experiments that have been made on the subject, to doubt: and it seems reasonable to expect, that a very refined or perfect chemistry will confirm the analogies of nature, and shew that bodies cannot be exactly the same in composition or chemical nature, and yet totally different in all their physical properties.